

PESTICIDE SURFACE WATER REPORT

FEBRUARY 2002 SAMPLING EVENT



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Pesticide Monitoring Project Report February 2002 Sampling Event

Executive Summary

As part of the District's quarterly ambient monitoring program, unfiltered water samples from 40 sites were collected from February 4 to February 6, 2002, and analyzed for over sixty pesticides and/or products of their degradation. The herbicides 2,4-D, ametryn, atrazine, bromacil, hexazinone, metolachlor, metribuzin, norflurazon, and simazine, along with the insecticides/degradates atrazine desethyl, atrazine desisopropyl, ethyl chlorpyrifos, alpha endosulfan, beta endosulfan, ethion, malathion, and metalaxyl were detected in one or more of these surface water samples.

The ethion concentrations of 0.021 µg/L at S176 exceeds the chronic toxicity level (0.003 µg/L) for *Daphnia magna* calculated according to promulgated procedure (FAC 62-302.200). *Daphnia magna* is a sensitive indicator species for aquatic macroinvertebrates. The only chlorpyrifos ethyl concentration detected (0.056 µg/L at S177), should not have an acute, detrimental impact on fish. However, for aquatic invertebrates, these levels are greater than the calculated acute and chronic toxicity (0.03 and 0.005 µg/L, respectively) for *Daphnia magna*. For both compounds, at these levels, long term exposure can cause impacts to macroinvertebrate populations, but the pulsed nature of agricultural runoff releases to the canal system precludes drawing any conclusions about the effects of long term average exposures.

The compounds and concentrations found are typical of those expected from intensive agricultural activity.

Background and Methods

The District's pesticide monitoring network includes stations designated in the Everglades National Park Memorandum of Agreement, the Miccosukee Tribe Memorandum of Agreement, the Lake Okeechobee Operating Permit, and the non-Everglades Construction Project (non-ECP) permit. The District's canals and marshes depicted in Figure 1 are protected as Class III (fishable and swimmable) waters, while Lake Okeechobee is protected as a Class I drinking water supply. Water Conservation Area 1 (WCA1) and the Everglades National Park are also designated as Outstanding Florida Waters, to which anti-degradation standards applies. Surface water and sediment are sampled quarterly and semiannually, respectively, upstream at each structure identified in the permit or agreement.

Sixty-six pesticides and degradation products were analyzed for in samples from all of the 40 sites (Figure 1). The analytes, their respective minimum detection limits (MDL), and practical quantitation limits (PQL) are listed in Table 1. All the analytical work is performed by the Florida Department of Environmental Protection (FDEP) Central Laboratory in Tallahassee Florida. The reader is referred to the *Quality Assurance Evaluation* section of this report for a summary of any limitations on data validity that might influence the utility of these data.

Each pesticide's description and possible uses and sites of application are taken from Hartley and

Kidd (1987). The Florida Ground Water Guidance Concentrations (FGWGC) (FDEP, 1994a) are listed to provide an indication at what level these pesticide residues could possibly impact human health, based on drinking water consumption or other routes of exposure (e.g., inhalation, ingestion of food residues, dermal uptake). Primary ground water standards are enforceable ground water standards, not screening tools or guidance levels. To evaluate the potential impacts on aquatic life, due to the pulsed nature of exposure, the maximum observed concentration is compared to the Criterion Maximum Concentration published by the USEPA under Section 304 (a) of the Clean Water Act, if available, or the lowest EC₅₀ or LC₅₀ reported in the summarized literature. This summary covers surface water samples collected from February 4 to February 6, 2002.

Findings and Recommendations

At least one pesticide was detected in surface water at 34 of the 40 sites. The concentrations of the pesticides detected at each of the sites are summarized for the surface water in Table 2. All of these compounds have previously been detected in this monitoring program.

The above findings must be considered with the caveat that pesticide concentrations in surface water and sediment may vary significantly in relation to the timing and magnitude of pesticide application, rainfall events, pumping and other factors, and that this was only one sampling event. The possible long term or chronic toxicity impacts are also reported based on the single sampling event and do not take into account previous monitoring data.

Usage and Water Quality Impacts

2,4-D: 2,4-D is a selective systemic herbicide used for the post-emergence control of annual and perennial broad leaf weeds in terrestrial (grassland, established turf, sugarcane, rice, and on non-crop areas) as well as aquatic areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that 2,4-D (1) has minimum loss from soil by surface adsorption, with a moderate loss by leaching and surface solution; (2) is slightly toxic to mammals and relatively non-toxic to fish; and (3) does not bioaccumulate significantly. The only 2,4-D concentration was detected at G94D (2.2 µg/L) (Table 2). Using these criteria, these levels should not have an acute impact on fish or aquatic invertebrates.

Ametryn: Ametryn is a selective terrestrial herbicide registered for use on sugarcane, bananas, pineapple, citrus, corn, and non-crop areas. Most algal effects occur at concentrations > 10 µg/L (Verschueren, 1983). Environmental fate and toxicity data in Tables 3 and 4 indicate that ametryn (1) is lost from soil relatively easily by leaching, surface adsorption, and in surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data includes a 96 hour LC₅₀ of 14.1 mg/L for goldfish (Hartley and Kidd, 1987). The ametryn surface water concentrations found in this sampling event ranged from 0.011 to 0.26 µg/L. Using these criteria, these surface water concentrations should not have an acute, detrimental impact on fish or aquatic invertebrates.

Atrazine: Atrazine is a selective systemic herbicide registered for use on pineapple, sugarcane, corn, rangelands, ornamental turf and lawn grasses, and non-crop areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that atrazine (1) is easily lost from soil by leaching and in

surface solution, with moderate loss from surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96 hour LC₅₀ of 76 mg/L for carp, 16 mg/L for perch and 4.3 mg/L for guppies (Hartley and Kidd, 1987). Also, in a flow-through bioassay, the maximum acceptable toxicant concentration (MATC) of atrazine was 90 and 210 µg/L for bluegill and fathead minnow (Verschuere, 1983). The atrazine surface water concentrations found in this sampling event at 21 of the 40 sampling locations, ranged from 0.0095 to 2.9 µg/L. Using these criteria, these levels should not have an acute or chronic detrimental impact on fish or invertebrates.

Atrazine desethyl (DEA) and atrazine desisopropyl (DIA) are biotic degradation products of atrazine. These degradation products are both persistent and mobile in water; however, DEA is more stable and the dominant initial metabolite. Since DEA and DIA are structurally and toxicologically similar to atrazine, the concentrations of total atrazine residue (atrazine + DEA + DIA) may also be a significant consideration in the surface water environment. The DEA to atrazine ratio (DAR), on a molar basis, has been suggested as an indicator of nonpoint-source pollution of groundwater (Adams and Thurman, 1991) and as a tracer of ground water discharge into rivers (Thurman et al., 1992). Goolsby et al. (1997) determined that low DAR values, median <0.1, occur in streams during runoff shortly after application of atrazine. Higher DAR values, median about 0.4, occur later in the year after considerable degradation of atrazine to DEA has occurred in the soil. The low DAR ratio (0.1) at the locations where both atrazine and DEA were detected, suggests minimum degradation of atrazine (Table 5). However, these general guidelines were developed based on observations in Midwest watersheds in northern temperate climates with different soil and water management regimes as well as higher atrazine water concentrations. Applications to the south Florida environment should be made with caution.

Bromacil: Bromacil is a terrestrial herbicide registered for use on pineapple, citrus, and non-crop areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that bromacil (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data includes a 96 hour LC₅₀ of 164 mg/L for carp (Hartley and Kidd, 1987). The highest concentration of bromacil detected in the surface water during this sampling event was at S79 (0.25 µg/L). Using these criteria, these levels should not have an acute or chronic detrimental impact on fish.

Chlorpyrifos ethyl: Chlorpyrifos ethyl is a non-systemic insecticide with contact, stomach, and respiratory action, for use on citrus, vegetables, rice, and household insect pests (Hartley and Kidd, 1987). Environmental fate and toxicity data in Tables 3 and 4 indicate that: chlorpyrifos ethyl (1) is not readily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is toxic to mammals and fish; and (3) bioconcentrates to a limited extent. The only concentration of chlorpyrifos ethyl found in this sampling event (0.056 µg/L at S177) could have an acute, harmful impact on aquatic invertebrates.

Endosulfan: Endosulfan is a non-systemic insecticide and acaricide registered for use on many crops, including beans, tomatoes, corn, cabbage, citrus, and ornamental plants. Technical

endosulfan is a mixture of the two stereoisomeric forms, the α (alpha) and the β (beta) forms. Endosulfan is highly toxic to mammals, with an acute oral LD₅₀ for rats of 70 mg/Kg (Hartley and Kidd, 1987). The Soil Conservation Service rates endosulfan with an extra small potential for loss due to leaching, a large potential for loss due to surface adsorption and a moderate potential for loss in surface solution (Table 3). β -endosulfan's water solubility and Henry's constant indicate volatilization may be significant in shallow waters. A bioconcentration factor of 1,267 indicates a low to moderate degree of accumulation in aquatic organisms (Lyman et al., 1990). Endosulfan (α and/or β) was detected at three locations (S176, S177, and S178) in the south Miami-Dade farming area (Table 2). However, these concentrations do not exceed the Florida Class III surface water quality standard (Chapter 62-302) (Figure 2).

Ethion: Ethion is a non-systemic acaricide and insecticide registered for use on several fruits, citrus, and vegetables. The use of ethion on citrus has been cancelled (Federal Register, March 22, 2002). By December 31, 2004, all use of existing stocks of the end-use products is prohibited. Environmental fate and toxicity data in Tables 3 and 4 indicate that ethion (1) is strongly sorbed to soil and therefore can accumulate in sediments; (2) is slightly toxic to mammals, relatively toxic to fish and extremely toxic to *Daphnia*; and (3) bioconcentrates to a limited extent. Several sources of toxicity information have shown both agreement and disagreement of these laboratory tests. The ethion concentration of 0.021 at S176, exceeds the chronic toxicity level (0.003 $\mu\text{g/L}$) for *Daphnia magna* calculated according to promulgated procedure (FAC 62-302.200). *Daphnia magna* is a sensitive indicator species for aquatic macroinvertebrates. At this level, long term exposure can cause impacts to macroinvertebrate populations, but the pulsed nature of agricultural runoff releases to the canal system precludes drawing any conclusions about the effects of long term average exposures. With the method detection limit around 0.019 $\mu\text{g/L}$, any detection will automatically exceed the calculated chronic toxicity (0.003 $\mu\text{g/L}$) for *Daphnia magna*.

Hexazinone: Hexazinone is a non-selective contact herbicide that inhibits photosynthesis. Registered uses include sugarcane, pineapple, and non-crop areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that hexazinone (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Hexazinone is practically non-toxic to freshwater invertebrates with an EC₅₀ of 145 mg/l for *Daphnia magna* (U.S. Environmental Protection Agency, 1988). The highest surface water concentration detected in this sampling event at S140 (0.11 $\mu\text{g/L}$) should not have an acute impact on fish or aquatic invertebrates.

Malathion: Malathion is an insecticide/acaricide used on a variety of crops including fruits, vines, ornamentals, vegetables, and field crops (Hartley and Kidd, 1987). Environmental fate and toxicity data in Tables 3 and 4 indicate that malathion (1) has a small potential for loss from soil by leaching, surface adsorption or surface solution; (2) is relatively non-toxic to mammals but highly toxic to fish; and (3) does not bioaccumulate significantly. The only concentration of malathion found in the surface water from this sampling event was 0.056 $\mu\text{g/L}$ at S99. This concentration is below the Florida Class III Water Quality Standard for surface water (Chapter

62-302) of 0.1 µg/L. Using these criteria, this level should not cause an acute, detrimental impact on fish or aquatic invertebrates.

Metalaxyl: Metalaxyl is a systemic fungicide. Registered uses include potatoes, strawberries, citrus, avocados and vegetables. Environmental fate and toxicity data in Tables 3 and 4 indicate that metalaxyl (1) is easily lost from soil by leaching and has a moderate potential for loss due to surface adsorption and surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioaccumulate significantly. The only concentration of metalaxyl detected was 0.058 µg/L at NSIDWC06 (Table 2). Using these criteria, the concentrations of metalaxyl detected should not have an acute, harmful impact on fish or aquatic invertebrates.

Metolachlor: Metolachlor is a selective herbicide used on potatoes, sugarcane, and some vegetables. Environmental fate and toxicity data in Tables 3 and 4 indicate that metolachlor (1) has a large potential for loss due to leaching and a medium potential for loss in surface solution and due to surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Metolachlor is non-toxic to birds (Lyman et al., 1990). The only surface water concentration found in this sampling event (0.12 µg/L at S5A) is over two orders of magnitude below the calculated chronic action level. Using these criteria, these levels should not have a harmful impact on fish or aquatic invertebrates.

Metribuzin: Metribuzin is a selective systemic herbicide used on a variety of crops including potatoes, tomatoes, sugarcane, and peas. Environmental fate and toxicity data in Tables 3 and 4 indicate that metribuzin (1) has a large potential for loss due to leaching, a medium potential for loss in surface solution, and a small potential for loss due to surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioaccumulate significantly. The only concentration of metribuzin detected was 0.027 µg/L (S178). Using these criteria, this surface water concentration should not have an acute impact on fish or aquatic invertebrates.

Norflurazon: Norflurazon is a selective herbicide registered for use on many crops including citrus. Environmental fate and toxicity data in Tables 3 and 4 indicate that norflurazon (1) is easily lost from soil surface solution and a moderate potential for loss due to leaching and surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. The LC₅₀ for norflurazon is >200 mg/L for catfish and goldfish (Hartley and Kidd, 1987). The norflurazon surface water concentrations ranged from 0.11 to 0.92 µg/L. Even at the highest concentration, this is several orders of magnitude below the calculated chronic action level. Using these criteria, these levels should not have an acute, detrimental impact on fish or aquatic invertebrates.

Simazine: Simazine is a selective systemic herbicide registered for use on many crops including sugarcane, citrus, corn, and non-crop areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that simazine (1) is easily lost from soil by leaching and has a moderate potential for loss due to surface adsorption and surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96 hour LC₅₀ of 49 mg/L for guppies (Hartley and Kidd, 1987). Most of the aquatic biological effects occur at concentrations > 500 µg/L (Verschueren, 1983). Aquatic invertebrate LC₅₀

toxicity ranges from 3.2 mg/L to 100 mg/L for simazine (U.S. Environmental Protection Agency, 1984). The highest surface water concentration of simazine was detected at S5A (0.27 µg/L), below any level of concern for fish or aquatic invertebrates.

Quality Assurance Evaluation

Replicate samples were collected at sites S3 and S178. All the analytes detected in the surface water had precision $\leq 30\%$ RPD. No analytes were detected in the field blanks collected at S2, S178, and S6. All samples were shipped and all bottles were received.

Low concentrations of representative analytes from each pesticide group/method were added to laboratory water as well as to samples submitted. The lab fortified blank, matrix spike recoveries, and precision for azinphos methyl did not meet the specified requirements for the surface water samples collected at the following locations: S18C S178, S177, S332, S176, S331, S178 (including replicates), US41-25, S12C, S355A, S355B, and G211. Matrix spike recoveries and precision for norflurazon were not assessed due to the high content of this parameter in the sample spiked for the following locations: S31, S9, G123, S142, S190, L3BRS, S8, S7, S99, GORDYRD, S80, S2 (including field blank), S3 (including replicates), and S4. Additionally, the lab fortified blank and matrix spike recoveries for ethoprop at the same locations did not meet the specified requirements. Matrix spike recoveries for aldrin, beta BHC, alpha endosulfan, heptachlor, heptachlor epoxide, as well as the lab fortified blanks for endosulfan sulfate and methoxychlor did not meet the specified requirements for the following locations: S38B, S6 (including field blank), NSIDWC06, NSIDWC07, S5A, ACME1DS, G94D, S79, CR33.5T, S78, S235, FECSR78, S65E, and S191. The remainder of the analytes for each sample adhered to the targets for precision and accuracy as outlined in the FDEP Comprehensive Quality Assurance Plan. Organic quality assurance targets are set according to historically generated data or are adapted from the U.S. Environmental Protection Agency with slight modifications or internal goals, based on FDEP limited data. Parameters with low or high recoveries indicate that the sample matrix interferes with these analyses and interpretation of the respective analytical results should consider this effect.

Glossary

- LD₅₀: The dosage which is lethal to 50% of the terrestrial animals tested within a short (acute) exposure period, usually 24 to 96 hours.
- LC₅₀: A concentration which is lethal to 50% of the aquatic animals tested within a short (acute) exposure period, usually 24 to 96 hours.
- EC₅₀: A concentration necessary for 50% of the aquatic species tested to exhibit a toxic effect short of mortality (e.g., swimming on side or upside down, cessation of swimming) within a short (acute) exposure period, usually 24 to 96 hours.
- Koc: The soil/sediment partition or sorption coefficient normalized to the fraction of organic carbon in the soil. This value provides an indication of the chemical's tendency to partition between soil organic carbon and water.

Bioconcentration Factor:

The ratio of the concentration of a contaminant in an aquatic organism to the concentration in water, after a specified period of exposure via water only. The duration of exposure should be sufficient to achieve a near steady-state condition.

Soil or water half-life:

The time required for one-half the concentration of the compound to be lost from the water or soil under the conditions of the test.

MDL: The minimum concentration of an analyte that can be detected with 99% confidence of its presence in the sample matrix.

PQL: The lowest level of quantitation that can be reliably achieved within specified limit of precision and accuracy during routine laboratory operating conditions. The PQL is further verified by analyzing spike concentrations whose relative standard deviation in 20 fortified water samples is < 15%. In general, the PQL is 2 to 5 times larger than the MDL.

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Table 1. Minimum detection limits (MDL) and practical quantitation limits (PQL) for pesticides determined in February 2002.

Pesticide or metabolite	Water Range of MDL-PQL (µg/L)	Pesticide or metabolite	Water Range of MDL-PQL (µg/L)
2,4-D	0.8 - 3.2	β-endosulfan (beta)	0.0038 - 0.016
2,4,5-T	0.8 - 16	endosulfan sulfate	0.0045 - 0.0192
2,4,5-TP (silvex)	0.8 - 3.2	endrin	0.019 - 0.228
alachlor	0.047 - 0.196	endrin aldehyde	0.0042 - 0.0176
aldrin	0.0019 - 0.04	ethion	0.019 - 0.076
ametryn	0.0094 - 0.0388	ethoprop	0.019 - 0.076
atrazine	0.0094 - 0.38	fenamiphos (nemacur)	0.028 - 0.116
atrazine desethyl	0.0094 - 0.0388	fonofos (dyfonate)	0.019 - 0.076
atrazine desisopropyl	0.0094 - 0.0388	heptachlor	0.0023 - 0.044
azinphos methyl (guthion)	0.019 - 0.076	heptachlor epoxide	0.0019 - 0.038
α-BHC (alpha)	0.0021 - 0.0088	hexazinone	0.019 - 0.076
β-BHC (beta)	0.0032 - 0.0136	imidacloprid	0.2 - 0.4
δ-BHC (delta)	0.0021 - 0.0088	linuron	0.2 - 0.4
γ-BHC (gamma) (lindane)	0.0019 - 0.038	malathion	0.028 - 0.116
bromacil	0.038 - 0.156	metalaxyl	0.047 - 0.196
butylate	0.019 - 0.076	methoxychlor	0.0038 - 0.2
carbophenothion (trithion)	0.015 - 0.064	metolachlor	0.057 - 0.232
chlordane	0.0094 - 0.04	metribuzin	0.019 - 0.076
chlorothalonil	0.015 - 0.064	mevinphos	0.057 - 0.232
chlorpyrifos ethyl	0.019 - 0.076	mirex	0.011 - 0.048
chlorpyrifos methyl	0.0094 - 0.0388	naled	0.075 - 0.312
cypermethrin	0.019 - 0.08	norflurazon	0.019 - 0.076
DDD-P,P'	0.0045 - 0.0192	parathion ethyl	0.019 - 0.076
DDE-P,P'	0.0038 - 0.016	parathion methyl	0.019 - 0.076
DDT-P,P'	0.0038 - 0.048	PCB	0.019 - 0.08
demeton	0.11 - 0.48	permethrin	0.015 - 0.064
diazinon	0.019 - 0.076	phorate	0.028 - 0.116
dicofol (kelthane)	0.042 - 0.176	prometryn	0.019 - 0.076
dieldrin	0.0019 - 0.038	simazine	0.0094 - 0.076
disulfoton	0.019 - 0.076	toxaphene	0.071 - 0.3
diuron	0.2 - 0.4	trifluralin	0.0075 - 0.092
α-endosulfan (alpha)	0.0038 - 0.016		

Table 2. Summary of pesticide residues (µg/L) in surface water samples collected by SFWMD in February 2002.

Date 2002	Site	Flow	2,4-D	ametryn	atrazine	atrazine desethyl	atrazine desisopropyl	bromacil	chlorpyrifos ethyl	endosulfan alpha	endosulfan beta	ethion	hexazinone	malathion	metalaxyl	metolachlor	metribuzin	norflurazon	simazine	Number of compounds detected at site
2/4	C25S99	N	-	-	-	-	-	-	-	-	-	-	-	0.056 I	-	-	-	0.78	0.090	3
	G211	Y	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	GORDYRD	Y	-	-	-	-	0.012 I	0.14 I	-	-	-	-	-	-	-	-	-	0.92	0.16	4
	S12C	N	-	-	0.031 I	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1
	S176	N	-	-	-	-	-	-	-	0.0098 I	-	0.021 I	-	-	-	-	-	-	-	2
	S177	N	-	-	-	-	-	-	0.056 I	0.028	0.0082 I	-	-	-	-	-	-	-	-	3
	S178	N	-	-	0.018 I *	-	-	-	-	0.015 I *	0.0147 I *	-	-	-	-	-	0.027 I *	-	-	4
	S18C	Y	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	S2	N	-	0.015 I	0.25	0.034 I	0.014 I	-	-	-	-	-	-	-	-	-	-	-	0.022 I	5
	S3	N	-	0.012 I *	0.20 *	0.032 I *	0.011 I *	-	-	-	-	-	-	-	-	-	-	-	0.019 I *	5
	S331	N	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	S332	N	-	-	-	-	-	-	-	0.0089 I	-	-	-	-	-	-	-	-	-	1
	S355A	N	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	S355B	N	-	-	0.012 I	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1
	S4	N	-	0.014 I	0.18	0.029 I	0.011 I	-	-	-	-	-	-	-	-	-	-	-	0.016 I	5
	S80	N	-	-	0.024 I	-	-	0.057 I	-	-	-	-	-	-	-	-	-	0.52	0.075	4
	US41-25	Y	-	-	0.10	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1
2/5	CR33.5T	N	-	0.026 I	0.32	0.021 I	0.012 I	0.21	-	-	-	-	0.020 I	-	-	-	-	0.23	0.059	8
	FECSR78	Y	-	0.018 I	0.065	-	-	0.067 I	-	-	-	-	-	-	-	-	-	0.060 I	-	4
	G123	N	-	-	0.0095 I	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1
	L3BRS	N	-	0.019 I	0.28	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2
	S140	N	-	-	0.053	-	-	-	-	-	-	-	0.11	-	-	-	-	0.038 I	0.015 I	4
	S142	N	-	0.011 I	0.021 I	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2
	S190	N	-	-	0.024 I	-	-	-	-	-	-	-	-	-	-	-	-	0.051	-	2
	S191	N	-	-	0.038	-	-	0.038 I	-	-	-	-	-	-	-	-	-	-	-	2
	S235	Y	-	0.030 I	0.19	0.032 I	0.012 I	-	-	-	-	-	0.021 I	-	-	-	-	-	0.020 I	6
	S31	Y	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	S65E	Y	-	-	0.092	0.016 I	-	0.053 I	-	-	-	-	-	-	-	-	-	-	0.022 I	4
	S7	N	-	0.019 I	0.14	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2
	S78	N	-	0.079	0.92	0.042	0.013 I	0.054 I	-	-	-	-	0.028 I	-	-	-	-	0.11	0.020 I	8
	S79	N	-	0.032 I	0.34	0.020 I	0.015 I	0.25	-	-	-	-	0.019 I	-	-	-	-	0.26	0.10	7
	S8	N	-	0.061	0.78	0.016 I	-	-	-	-	-	-	-	-	-	-	-	-	-	3
	S9	Y	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0
2/6	ACME1DS	N	-	0.013 I	0.033 I	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2
	G94D	N	2.2 I	0.013 I	0.029 I	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3
	NSIDWC06	N	-	0.014 I	1.5	0.084	0.015 I	-	-	-	-	-	-	-	0.058 I	-	-	-	0.011 I	6
	NSIDWC07	N	-	0.020 I	2.9	0.17	0.032 I	-	-	-	-	-	-	-	-	-	-	-	0.014 I	5
	S38B	N	-	0.018 I	0.99	0.078	0.014 I	-	-	-	-	-	-	-	-	-	-	-	-	4
	S5A	N	-	0.071	0.62	0.020 I	-	-	-	-	-	-	0.022 I	-	-	0.12 I	-	-	0.27	6
	S6	N	-	0.26	1.0	0.012 I	-	-	-	-	-	-	0.021 I	-	-	-	-	-	-	4
Total number of compound detections			1	19	29	14	11	8	1	4	2	1	7	1	1	1	1	6	15	

N – no Y – yes R – reverse ; - denotes that the result is below the MDL; * - results are the average of duplicate samples; I - value reported is less than the minimum quantitation limit, and greater than or equal to the minimum detection limit

Table 3. Selected properties of pesticides found in February 2002 sampling event

common name	Surface Water Standards 62-302 (µg/L)	Ground Water Guidance Conc. (µg/L)	LD50 acute rats oral (mg/kg) (1)	EPA carcinogenic potential	Water Solubility (mg/L) (2, 3)	Koc (mL/g) (2, 3)	soil half-life (days) (2, 3)	SCS rating (2)			Bioconcentration Factor (BCF)
								LE	SA	SS	
2,4-D (acid)	(100)	70**	375	D	890	20	10	M	S	M	13
ametryn	-	63	1110	D	185	300	60	M	M	M	33
atrazine	-	3**	3080	C	33	100	60	L	M	L	86
bromacil	-	90	5200	C	700	32	60	L	M	M	15
chlorpyrifos ethyl	-	21	135 - 163	D	2	6070	30	S	M	M	418
endosulfan alpha	0.056	0.35	70	-	0.53	12400	50	XS	L	M	884
endosulfan beta	-	0.35	70	-	0.28	-	-	-	-	-	1267
ethion	-	3.5	208	-	1.1	8900	150	S	L	M	586
hexazinone	-	231	1690	D	33000	54	90	L	M	M	2
malathion	0.1	140	2800	D	145	1800	1	S	S	S	37
metalaxyl	-	420	669	-	7100	100	70	L	M	M	4
metolachlor	-	1050	2780	C	530	200	90	L	M	M	18
metribuzin	-	175	2200	D	1220	41	30	L	S	M	11
norflurazon	-	280	9400	C	28	700	90	M	M	L	94
simazine	-	4**	>5000	C	6.2	130	60	L	M	M	221

SCS Ratings are pesticide loss due to leaching (LE), surface adsorption (SA) or surface solution (SS) and grouped as large(L), medium (M), small (S) or extra small (XS)

Volatility from water: R = rapid, I = insignificant, S = significant

Bioconcentration Factor (BCF) calculated as $BCF = 10^{(2.791 - 0.564 \log WS)}$ (4)

B2: probable human carcinogen; C: possible human carcinogen; D: not classified; E: evidence of non-carcinogen for humans (5)

FDEP surface water standards (4/95) for Class III waters except Class I in ()

Copper 6.5 µg/L when hardness = 50 mg/L

Note: endosulfan usually considered the sum of alpha and beta isomers

** primary standard

(1) Hartley, D. and H. Kidd. (Eds.) (1987)

(2) Goss, D. and R. Wauchope. (Eds.) (1992)

(3) Montgomery, J.H. (1993)

(4) Lyman, W.J., W.F. Reehl, and D.H. Rosenblatt. (1990)

(5) U.S. Environmental Protection Agency (1996)

Table 4. Toxicity of pesticides found in the February 2002 sampling event to freshwater aquatic invertebrates and fishes (µg/L).

common name	48 hr EC50		acute toxicity (*)	chronic toxicity (*)	96 hr LC50		acute toxicity	chronic toxicity	96 hr LC50		acute toxicity	chronic toxicity	96 hr LC50		acute toxicity	chronic toxicity	96 hr LC50		acute toxicity	chronic toxicity	96 hr LC50		acute toxicity	chronic toxicity
	Water flea <i>Daphnia magna</i>				Fathead Minnow (#) <i>Pimephales promelas</i>				Bluegill <i>Lepomis macrochirus</i>				Largemouth Bass <i>Micropterus salmoides</i>				Rainbow Trout (#) <i>Oncorhynchus mykiss</i>				Channel Catfish <i>Ictalurus punctatus</i>			
2,4-D	25,000	(9)	8333	1250	133,000	(9)	44,333	6650	180,000	(10)	60000	9000	-		-	-	100,000	(6)	33333	5000	-		-	-
	-		-	-	-		-	-	900 (48 hr)	(8)	-	-	-		-	-	110,000	(9)	36667	5500	-		-	-
ametryn	28,000	(9)	9333	1400	-		-	-	4,100	(6)	1367	205	-		-	-	8,800	(6)	2933	440	-		-	-
atrazine	6900	(9)	2300	345	15,000	(9)	5000	750	16,000	(6)	5333	800	-		-	-	8,800	(6)	2933	440	7,600	(6)	2533	380
bromacil	-		-	-	-		-	-	127,000	(9)	42333	6350	-		-	-	36,000	(9)	12000	1800	-		-	-
chlorpyrifos ethyl	1.7	(9)	0.57	0.085	203	(9)	68	10	2.6	(6)	0.87	0.13	-		-	-	11	(6)	3.7	0.55	280	(9)	93	14
	0.1	(9)	0.03	0.005	-		-	-	5.8	(9)	1.93	0.29	-		-	-	-		-	-	-		-	-
endosulfan	166	(9)	55	8	1	(1)	0.3	0.05	1	(1)	0.33	0.05	-		-	-	1	(1)	0.33	0.050	1	(1)	0.3	0.05
	-		-	-	-		-	-	2	(4)	0.67	0.10	-		-	-	3	(2)	1	0.15	1.5	(9)	0.5	0.08
	-		-	-	-		-	-	-		-	-	-		-	-	1	(4)	0.33	0.050	-		-	-
	-		-	-	-		-	-	-		-	-	-		-	-	0.3	(7)	0.10	0.015	-		-	-
ethion	0.06	(1)	0.02	0.003	720	(1)	240	36	210	(1)	70	11	173	(1)	58	9	500	(1)	167	25	7,600	(1)	2533	380
	-		-	-	-		-	-	13	(4)	4.3	0.65	150	(5)	50	8	193	(4)	64	10	7,500	(5)	2500	375
	-		-	-	-		-	-	22	(5)	7.3	1.1	-		-	-	560	(5)	187	28	-		-	-
hexazinone	151,600	(9)	50533	7580	274,000	(6)	91333	13700	100,000	(9)	33333	5000	-		-	-	180,000	(9)	60000	9000	-		-	-
malathion	1	(1)	0.3	0.05	8,650	(1)	2883	433	103	(1)	34	5.2	285	(1)	95	14	200	(1)	67	10	8,970	(1)	2990	449
	1.8	(5)	0.6	0.09	9,000	(2)	3000	450	110	(2)	37	5.5	-		-	-	170	(2)	57	9	7,620	(9)	2540	381
	-		-	-	-		-	-	12	(3)	4	0.6	-		-	-	100	(3)	33	5	-		-	-
	-		-	-	-		-	-	-		-	-	-		-	-	29	(4)	10	1.5	-		-	-
metalaxyl	28,000	(9)	9333	1400	-		-	-	139,000	(9)	46333	6950	-		-	-	132,000	(9)	44000	6600	-		-	-
metolachlor	23,500	(9)	7833	1175	-		-	-	15,000	(6)	5000	750	-		-	-	2,000	(6)	667	100	4,900	(7)	1633	245
metribuzin	4,200	(9)	1400	210	-		-	-	80,000	(6)	26667	4000	-		-	-	64,000	(6)	21333	3200	100,000	(9)	33333	5000
norflurazon	15,000	(9)	5000	750	-		-	-	16,300	(9)	5433	815	-		-	-	8,100	(9)	2700	405	>200,000	(6)	>67,000	>10,000
simazine	1,100	(9)	367	55	100,000	(9)	33333	5000	90,000	(6)	30000	4500	-		-	-	100,000	(9)	33333	5000	-		-	-

(*) Florida Administrative Code (FAC) 62-302.200, for compounds not specifically listed, acute and chronic toxicity standards are calculated as one-third and one-twentieth,

respectively, of the amount lethal to 50% of the test organisms in 96 hours, where the 96 hour LC50 is the lowest value which has been determined for a species significant to the indigenous aquatic community.

(#) Species is not indigenous. Information is given for comparison purposes only.

(1) Johnson, W. W. and M.T. Finley (1980)

(2) U.S. Environmental Protection Agency (1977)

(3) Davis, R. A. (Ed.) (1970)

(4) Schneider, B.A. (Ed.) (1979)

(5) U.S. Environmental Protection Agency (1972)

(6) Hartley, D. and H. Kidd. (Eds.) (1987)

(7) Montgomery, J.H. (1993)

(8) Verschueren, K. (1983)

(9) U.S. Environmental Protection Agency (1991)

(10) Mayer, F.L., and M.R. Ellersieck. (1986)

Table 5. Atrazine Desethyl/Atrazine ratio (DAR) data February 2002

Date	Site	Flow*	atrazine ug/L	moles/L	atrazine desethyl ug/L	moles/L	DAR
2/4/2002	S2	N	0.25	1.16E-09	0.034	1.81E-10	0.2
	S3**	N	0.20	9.27E-10	0.032	1.71E-10	0.2
	S4	N	0.18	8.35E-10	0.029	1.55E-10	0.2
2/5/2002	CR33.5T	N	0.32	1.48E-09	0.021	1.12E-10	0.1
	S235	Y	0.19	8.81E-10	0.032	1.71E-10	0.2
	S65E	Y	0.092	4.27E-10	0.016	8.53E-11	0.2
	S78	N	0.92	4.27E-09	0.042	2.24E-10	0.1
	S79	N	0.34	1.58E-09	0.020	1.07E-10	0.1
	S8	N	0.78	3.62E-09	0.016	8.53E-11	0.0
2/6/2002	NSIDWC06	N	1.5	6.95E-09	0.084	4.48E-10	0.1
	NSIDWC07	N	2.9	1.34E-08	0.17	9.06E-10	0.1
	S38B	N	0.99	4.59E-09	0.078	4.16E-10	0.1
	S5A	N	0.62	2.87E-09	0.020	1.07E-10	0.0
	S6	N	1.0	4.64E-09	0.012	6.40E-11	0.0
				DAR	All sites	Flow only sites	No flow sites
				average	0.1	0.2	0.1
				median	0.1	0.2	0.1
				minimum	0.0	0.2	0.0
				maximum	0.2	0.2	0.2

** Average of the replicate samples

* N-no; Y=yes;

Figure 2. Endosulfan Concentration in Surface Water at S178

